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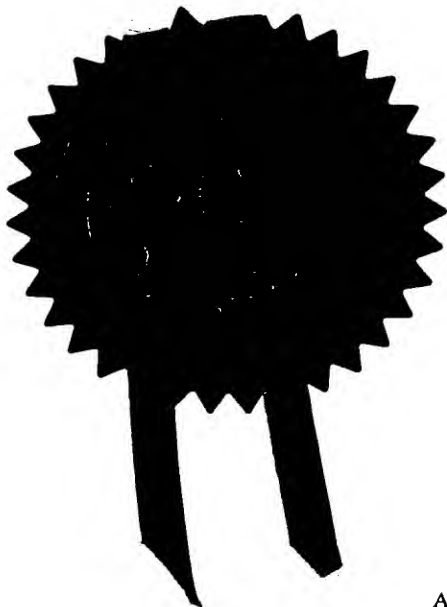
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P. Mahoney

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AA 1477 GB

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2. Patent application number

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3. Full name, address and postcode of the or of each applicant (underline all surnames)

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LONDON SW1 5BQ

Patents ADP number (if you know it)

If the applicant is a corporate body, give the country/state of its incorporation

GB

536268007 IS

4. Title of the invention

EMISSION CONTROL

5. Name of your agent (if you have one)

IAN CARMICHAEL WISHART

"Address for service" in the United Kingdom to which all correspondence should be sent (including the pc. code)

JOHNSON MATTHEY TECHNOLOGY CENTRE
BLOUNTS COURT
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Country

Priority application number
(if you know it)Date of filing
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GB

9822083.3

12 OCT 98

7. If this application is divided or otherwise derived from an earlier UK application, give the number and the filing date of the earlier application

Number of earlier application

Date of filing
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8. Is a statement of inventorship and of right to grant of a patent required in support of this request? (Answer 'Yes' if:

YES

- a) any applicant named in part 3 is not an inventor, or
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Description

Claim(s)

3

Abstract

1

Drawing(s)

1

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Priority documents

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Statement of inventorship and right to grant of a patent (Patents Form 7/77)

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DUPLICATE

EMISSION CONTROL

This invention concerns emission control systems, especially for diesel, i.e compression-ignition, engine exhausts.

EP-A-0341832 describes a process and treatment system for removing soot from diesel exhaust gas containing NO by passing such gas unfiltered over an oxidation catalyst to convert NO to NO₂, collecting the soot on a filter and using the gas containing NO₂ to combust the collected soot, the amount of NO converted to NO₂ being sufficient to enable such combustion to proceed at a temperature less than 400°C.

EP-A-0758713 describes a process in which a soot combustion step is followed by removing NO_x from the combustion outlet gas by means of a solid absorbent and regenerating the absorbent with rich exhaust gas obtained by intermittent alteration of the exhaust gas composition by engine fuel inlet adjustment or injection of reductant into the exhaust gas upstream of the oxidation catalyst. This process has disadvantages, for example requiring engine modification.

In co-pending GB application 9822083.3, from which the present application claims priority, there is described a process for treating combustion exhaust gas containing CO, HC, NO, O₂, soot and non-reactive gases, by the steps:

- i. catalysing oxidation of said NO to NO₂;
- ii. collecting soot on a filter from the product of i;
- iii. combusting said soot by reaction with said NO₂ and possibly also any O₂ left over after the reactions in i;
- iv. removing NO_x from the product of iii by the action of a regenerable NO_x absorbent; and
- v. regenerating said absorbent by intermittently decreasing the net oxidant level upstream of said oxidation catalyst;
- vi. at least during said regeneration, passing the gas leaving the absorbent over a catalyst system effective to promote reactions of HC and CO with O₂ to H₂O and CO₂ and preferably also to react NO_x to N₂.

That application describes also a treatment system for such exhaust gas corresponding to those process steps. It particularly describes processes using reductant injection downstream of said filter and processes using a NOx-specific reactant such as ammonia. The present application discloses further aspects and preferred features of that invention. For the present application the catalysts, filter and NOx absorber are broadly as in the co-pending application.

In a preferred form of the process, step v comprises: v. regenerating said absorbent by intermittently decreasing the net oxidant level by injecting reductant upstream of said absorber but downstream of said oxidation catalyst.

In this preferred form of the invention, injection of fuel upstream of the oxidation catalyst to provide for reaction increasing gas temperature is not excluded, but is controlled to give gas lean enough for absorption of NOx to continue. The fuel injection downstream of the oxidation catalyst decreases the oxidant content to a NOx desorption level.

In a further aspect the invention step v comprises: v. regenerating said absorbent by intermittently injecting a NOx-specific reactant upstream of said absorbent.

For regeneration using a NOx-specific reactant, the oxidant level can be decreased less, if at all, than when using a non-specific reductant such as hydrocarbon, hydrogen or dehydrogenatable organic compound reductant, as set forth in the co-pending application. The air/fuel weight ratio range 10 to equivalence indicated therein is a preference for such non-specific reductants. The further aspect of the invention includes the use of NOx-specific reactants especially in lean conditions, for example:

- (a) exhaust gas as generated by the engine or as issuing from a preceding step of exhaust treatment;
- (b) such gas to which reductant short of equivalence has been or is being added; and
- (c) gas made leaner, for example when the NOx-specific reactant is injected with the aid of air.

As disclosed in the co-pending application, the NOx-specific reactant may be nitrogen hydride for example ammonia or hydrazine, and can be injected as such or as a solution in eg water or as a precursor compound producing the reactant in exhaust treatment conditions, for example urea or aqueous urea solution. Such compounds act by providing

ammonia or hydrazine and are referred to herein as 'ammonia' at stages after injection. Injectors for such reactants or compounds, possibly using carrier gas such as air, have been published.

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The point of injection of the reactant may most simply be downstream of the filter. In this event the temperature is typically in the range 150° to 300°C.

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However, injection may be earlier, if upstream of the filter but downstream of the oxidation catalyst, the temperature is typically in the range 250° to 350°C at filter inlet, as required for adequate rate of soot combustion. Further, the reactant may be injected upstream of the oxidation catalyst.

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Since in such earlier injection the fed reactant is at a 'spike' concentration to react with NOx to be evolved over the short period of regeneration of the downstream NOx absorber, it is in substantial excess over the NOx in the flowing exhaust gas and consequently need not suffer much loss by reaction with NOx. If in an extreme case it were to react with all the flowing NOx to give N₂ or N₂O, this would stop combustion of soot on the filter: however owing to the shortness of the ammonia injection spike, any accumulation of soot would be small and combustion would be resumed before blockage took place. The temperature should not be high enough to give substantial oxidation of ammonia to NOx over the oxidation catalyst. To limit unwanted side-reactions of ammonia, it may be introduced as a precursor compound, thus delaying availability of ammonia. Such limitation may also be provided by suitable formulation of the oxidation catalyst and/or filter. In particular, the filter may be of the non-catalysed type, free of deliberately introduced catalytic material such as PGM. Any fortuitous catalytic activity of the filter, due for example to its structural material or to accumulated deposits such as carbon, appears not to seriously promote such side-reactions.

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The rate of provision of the reactant for steps v and vi should be as nearly as possible stoichiometric to the quantity of NOx to be reacted. Especially when injection is upstream of the filter, the rate should be controlled in response to measurements of final exit NOx and ammonia.

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In the process using the reactant there may also be enrichment of the gas by introduction of non-specific reductant.

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As in the co-pending application in the NOx adsorber ('NOx trap') the absorbent is preferably catalysed. By 'catalysed' is meant that the absorbent is intimately associated with catalytic material effective for the reaction of ammonia with NOx. Such material may be for example co-recipitated or co-impregnated or co-deposited with NOx absorbent or present as one or more sandwiched layers or as a fine (eg 10-500 microns) particles on or in a layer of absorbent or among particles of absorbent. The catalytic agents can be for example oxides such as vanadia/titania or precious metals such as PGMs and are effective to promote such reactions as the interchanges of the nitrogen oxides and the reaction with ammonia.

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Instead of or in addition to catalyst associated with the absorbent, there may be a step of, at least during said regeneration, passing the gas from the absorbent over a catalyst system effective to promote reactions of HC and CO with O₂ to H₂O and CO₂. Preferably the catalyst system is effective also to react NOx to N₂.

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Control of the process includes for example:

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1. response to NOx or ammonia leakage from the absorber and / or final exit gas;
2. response to prediction based on input of data on deliberate or load-responsive engine management variation;
3. allowance for gas composition variations, for example non-steady conditions such as incomplete warm-up, variation in load or weather. In particular, injection is timed to occur when the temperature is at a level permitting regeneration.

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Usually the regeneration phase can be a small fraction of engine running time, eg 0.1% to 5%, depending of course on operating conditions.

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The invention provides also a system corresponding to the process steps an engine in combination with such a system and a process of operating such an engine. The combination may include expedients such as electric heating, EGR, or recycle of released NO_x to one or more points upstream of the soot filter.

The combination may include sensors for at least one of:

fuel composition;

air/fuel ratio at engine inlet;

exhaust gas compositions and temperatures at critical stages;

pressure drop, especially over the filter.

It may include also indicator means informing the engine operator, computer means effective to evaluate the data from the sensor(s), and control linkages effective to adjust the engine to desired operating conditions taking account of eg. start-up, varying load and chance fluctuations.

Preferably the engine is a diesel engine, although other engines, including direct injection gasoline engines, may also benefit from the invention. The engine may be the motive power for a vehicle, or may be a stationary power source or auxiliary power source. It may be for a 'heavy duty' vehicle, ie at least 3500 Kg, or a 'light duty' vehicle, including in particular a passenger car or light van and likely to be operated according to the 'urban cycle'.

Desirably, the engine is fuelled with low-sulphur fuel, i.e having less than 50 especially less than 10, ppm of sulphur, by weight as elemental S. For operation with higher sulphur fuels, a SOx absorbent may be used at some stage upstream of the NOx absorber.

The invention is illustrated by the accompanying schematic drawing of a reactor providing a system for carrying out the process.

Referring to the drawing, items 10 to 30 are as described in the co-pending application, except for these modifications:

(a) injector 18 receives gaseous ammonia;

(b) pump 24 feeds ammonia at a rate stoichiometrically equivalent to the NOx to be released; and

(c) catalyst 30 is an SCR catalyst. If desired, absorber 28 and SCR catalyst 30 may be adjacent or mixed together on a single honeycomb.

The process and system of the invention is expected to be capable of meeting European Stage IV emission legislation, as published in Directive 98/69/EC with all regulated emissions comfortably within the standards set.

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Example 1 - NOx-Trap Regeneration with Diesel Fuel
(as in the co-pending application)

A NOx-trap comprising a 400 cpsi monolith having wall thickness of 6/1000 of an inch, measuring 5.66 x 6 inches, carrying a coating containing barium oxide (13.2%), platinum (1.7%), rhodium (0.17%), with minor proportions of alumina, ceria and zirconia with a total loading of 3.5 g/in³ was subjected to a gas stream from a 1.9 litre naturally aspirated direct injection diesel engine (Swedish MK-1 fuel) containing NOx (260 ppm) at a catalyst inlet temperature of 310C for 30 seconds during which time it began to become saturated with stored NOx. Upon introduction of diesel fuel into the exhaust gas stream in front of the NOx-trap at a rate of 1 g/s for 3 seconds, the NOx-trap regenerated, such that it was able to store NOx once more. The original operating conditions were restored whereby the same amount of NOx was stored, and this process was repeated many times without deterioration of the NOx capacity of the trap.

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Example 2 - NOx-Trap Regeneration with EGR + Fuel Injection
(as in the co-pending application)

A NOx-trap as Example 1 was subjected to a gas stream containing NOx (145 ppm) at a catalyst inlet temperature of 220°C for 30 seconds during which time it stored NOx. The engine was as in Example 1, except for use of EGR to reduce the oxygen concentration in the gas stream. Diesel fuel was introduced into the gas stream in front of the NOx-trap at a rate of 1 g/s for 1.5 seconds, to regenerate the NOx-trap; it was able to store NOx once more. The original operating conditions were restored whereby the same amount of NOx was stored, and this process was repeated many times without deterioration of the NOx capacity of the trap.

Analogous successful runs were performed at other temperatures between 180°C and 330°C, with fuel injection for different times.

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Example 3 - NO_x-Trap Regeneration with Ammonia**(part a as in the co-pending application)**

5 (a) A NO_x-trap as Example 1, but also including palladium (1.7%) was subjected to a synthetic gas stream containing NO_x (100 ppm), O₂ (9.55%), CO₂ (8.2%) and H₂O (9%) at a succession of catalyst inlet temperatures from 200° to 300°C for 60 seconds during which time it began to saturate with stored NO_x. Upon introduction of ammonia (500 ppm) and cutting off O₂ to give a reductant rich gas stream for 60 seconds, the NO_x-trap regenerated,
10 such that it was able to store NO_x once more. The original operating conditions were restored as Example 1.

(b) The run described in paragraph (a) was repeated but with the difference that for each temperature level the flow of gas was maintained with O₂ feed cut off and with
15 ammonia injection long enough to stabilise the temperature; this also fully regenerated the NO_x absorber. Then the O₂ feed was resumed and a 300-second run in lean conditions carried out. In each such run, 60-second periods were alternated: absorption, without ammonia injection; and regeneration, with ammonia injection.

20 Successive 300-second runs were carried out at stepped temperatures. The outlet NO_x contents ppm v/v were:

150°-170°C: 30-40

200°C: 30

250°C: 25

300°C: 25 rising to 45

350°C: 25 rising to 100

It is evident that at over 300°C there is considerable side reaction of ammonia to
30 NO_x. However, at 150°-300°C absorption of NO_x and regeneration by ammonia are effective, even in the presence of the O₂.

(c) By way of illustrating injection of ammonia upstream of the filter and use of the ammonia precursor urea, a part-system consisting of item 14 (oxidation catalyst) and item 16
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(non-catalysed cordierite soot filter), as described in the co-pending application, was set up and equipped between 14 and 16 with a sparging spray injector fed from a reservoir of 32%w/w aqueous urea. The system included sensors for NO_x and NO at engine outlet and 16 outlet. The inlet of 14 was fed with the exhaust of a 10 litre Volvo Diesel engine. NO_x levels were measured initially without urea injection, then at intervals during urea injection at approximately equivalence to the NO_x in the gas as received, then after stopping urea injection. Runs were carried out at temperatures in the range of 225°-350°C. Gas analyses for 290°C may be regarded as typical, and were as follows.

(measured in ppm)

	NO _x	NO	NO ₂
Engine out	540	505	35
16 Out (no Urea)	525	200	325
16 Out (urea)	400	160	240
16 out (urea stopped)	520	170	350

It is evident that injection of urea has decreased the NO_x content of the gas by only about 25%, leaving about 75% of the urea-derived ammonia available for use downstream of filter 16. In a system in which ammonia is to regenerate a NO_x absorber, the ration of ammonia to NO_x at the inlet of 16 would be a 'spike', ie. much higher than stoichiometric and fully enough ammonia would reach the NO_x absorber. Likewise, such a spike of ammonia, especially if added as urea, would sufficiently escape reaction over oxidation catalyst 14.

CLAIMS

A process for treating combustion exhaust gas containing CO, HC, NO, O₂, soot and non-reactive gases. by the steps:

- i. catalysing oxidation of said NO to NO₂;
- ii. collecting soot on a filter from the product of i;
- iii. combusting said soot by reaction with said NO₂ and possibly also any O₂ left over after the reactions in i;
- iv. removing NO_x from the product of iii by the action of a regenerable NO_x absorbent; and
- v. regenerating said absorbent intermittently;
- vi. at least during said regeneration, passing the gas leaving the absorbent over a catalyst system effective to promote reactions of HC and CO to H₂O and CO₂ and of NO_x to N₂.; characterised in that said regeneration comprises:
 - (a) decreasing the net oxidant level by injecting reductant upstream of said absorber but downstream of said oxidation catalyst; and/or
 - (b) injecting a NO_x-specific reactant upstream of said absorbent.

2. Process according to claim 1 in which the NO_x absorber comprises:

- (a) compounds of alkali metals, alkaline earth metals, rare earth metals and transition metals, capable of forming nitrates and/or nitrites of adequate stability in absorbing conditions and of evolving nitrogen oxides and/or nitrogen in regenerating conditions;
- (b) adsorptive materials such as zeolites, carbons and high-area oxides.

3. Process according to Claim 1 or claim 2 in which the absorber is catalysed.

4. Process according to any area of the preceding claims in which the catalyst associated with the adsorber comprises Vanadia/Titania and/or one or more platinum group metals.

5. Process according to any one of the preceding claims in which reductant or reactant is introduced after step iii.

6. Process according to any one of the preceding claims in which the reductant is hydrocarbon, hydrogen or dehydrogenatable organic compound.
- 5 7. Process according to claim 6 in which air/fuel weight ratio of the exhaust gas containing said injected reductant is in the range 10 to equivalence.
8. Process according to any one of claims 1 to 5 in which the NO_x-specific reactant is a nitrogen hydride and is injected as such and/or as a precursor compound decomposable thereto in situ.
- 10 9. Process according to claim 8 in which ammonia is injected as urea or aqueous urea solution.
- 15 10. Process according to claim 8 or claim 9 in which the reactant is injected into:
(a) exhaust gas as generated by the engine or as issuing from a preceding step of exhaust treatment; or
(b) such gas to which reductant short of equivalence has been or is being added; or
(c) gas made leaner, for example when the NO_x-specific reactant is injected with the aid of compressed air.
- 20 11. Process according to claim 12 or claim 13 in which the reactant is injected upstream of the filter.
- 25 12. Process according to claim 11 in which the filter is non-catalysed.
13. Process according to claim 14 in which the reactant is injected upstream of the oxidation catalyst
- 30 14. Process according to any one of the preceding claims in which the exhaust gas is the product of combustion of a fuel containing less than 50 ppm w/w of sulphur.
15. System for treatment of combustion exhaust gas having integers corresponding to the process according to any one of the preceding claims.

16. A diesel engine having a system according to claim 15 connected to its exhaust.

17. An engine according to claim 16 which is of the turbo-charged direct injection type.

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18. A process, system or engine according (as appropriate) to any one of the preceding claims, including sensors, indicators, computers and actuators, effective to maintain operation within desired conditions.

10 19. A process, system or engine substantially as described and as illustrated by the foregoing specific description.

20. A process, system or engine according (as appropriate) to any one of the preceding claims, operated in compliance with the European Stage IV emission legislation.

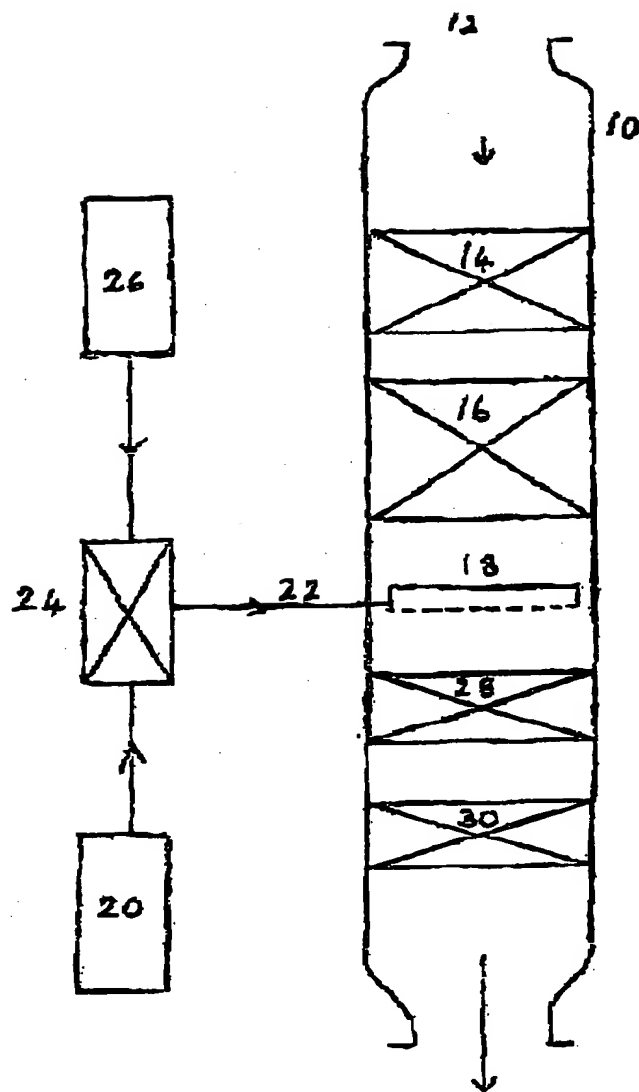
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EMISSION CONTROL**Abstract of the Invention**

- 15 A process for treating combustion gases, e.g. from a diesel engine, by catalytic oxidation of NO to NO₂, trapping soot and thereafter combusting soot using reaction with NO₂ and absorbing NO_x from the gases resulting from the combustion, is characterised in that the NO_x absorbent is regenerated by decreasing the net oxident level by injecting reductant upstream of the absorber but downstream of the oxidation catalyst and/or by injecting a
- 20 NO_x-specific reactant upstream of the absorbent.



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